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(54) FLAME-RETARDANT RESIN COMPOSITION CONTAINING POLYSTYRENE OBTAINED BY ANIONIC POLYMERIZATION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a flame-retardant styrene resin composition excellent in a balance between flowability and impact resistance by mixing a rubber-modified vinylaromatic polymer in which the continuous phase comprises a resin containing a vinylaromatic polymer obtained by anionic polymerization with a flame retardant.

SOLUTION: This composition comprises 99-50 pts.wt. rubber-modified vinylaromatic polymer (A) which is obtained by radical polymerization and in which the continuous phase comprises a resin containing a linear or branched vinylaromatic polymer obtained by anionic polymerization and 1-50 pts.wt. halogenated flame retardant or a mixture thereof with an antimony oxide or phosphorus flame retardant. The linear vinylaromatic polymer of component A should have a ratio of the weight-average molecular weight to the number-average ratio of 2.0 or below when determined by the gel permeation chromatography differential refractometry and have a weight-average molecular weight of 50,000-200,000. Also the branched vinylaromatic polymer of component A has restrictions on its molecular structure.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the styrene system fire retardancy resin constituent which can be used as molding materials, such as the various mold goods of which fire retardancy is required, for example, home electronics, OA machine, and autoparts, about the styrene system fire retardancy resin constituent excellent in the balance of a fluidity and impact strength-proof.

[0002]

[Description of the Prior Art] Styrene resin is widely used industrially as a cheap molding material excellent in workability and various physical properties. In the molding material application of the light electric appliance machine field, a fire-resistant demand is high and it especially applies also for many flameproofing techniques of styrene resin. For example, the approach (JP,52-32898,B) using a halogen series flame retardant, and the combination (JP,1-182342,A) of antimony oxide and decabromodiphenyl ether as a flame retarder, the approach (JP,58-65741,A official report) of carrying out the amount combination of specification of the antimony trioxide by concomitant use of halogenation diphenyl ether and halogenation bisphenol mold polycarbonate oligomer, etc. are mentioned.

[0003] However, since the fall of physical properties, especially the remarkable fall of shock-proof reinforcement would be caused if flameproofing of the polystyrene system resin is carried out by these approaches, or a fluidity got worse to the degree of pole depending on the flame retarder to be used, a fire-resistant resin constituent excellent in shock-proof and fluid balance was desired. In addition, in order that the request of enlargement and thinning may increase and home electronics may fill these requests, improvement and high fluidization of the mechanical strength of resin are searched for in recent years. Melting dropping at the time of combustion is made easy to cause at the same time the approach of adding plasticizers, such as a mineral oil generally used, reduces fire retardancy, in order to attain high fluidization of resin.

[0004] For example, are required of the housing ingredient in which injection molding is possible with the low voltage of wide mold large-sized television (28 32 or 36 inches). The fire-resistant molding material specified by the specification of UL94V-0 of a high flow (MFR30g / 10 min or more) As usual high impact polystyrene, high fluidity polystyrene, and a flame retarder, a bromine-ized epoxy resin, In order to satisfy the fluidity required as it compounding using a paraffin series mineral oil etc. as a fluid amelioration agent, it is necessary to add a mineral oil more than 4 - 6 weight section to the resin section 100 weight section. Addition of a lot of mineral oils imitates a heat-resistant fall sharp naturally, comes, and brings about the fall of the mechanical strength of resin.

[0005] Furthermore, in the UL94verticalburning test about fire retardancy, at the time of combustion, dropping is severe, and achievement is difficult for the fire-resistant engine performance of V-O specification, therefore, as for this ingredient, there is a limitation in the approach of improving the fluidity of resin by addition of plasticizers, such as a mineral oil. Moreover, although the method of achieving low-molecular-weight-ization of a resin matrix in order to achieve high fluidization of resin is taken, since it will become still weaker if it becomes very difficult to maintain the mechanical strength of a resin constituent and fluid balance and flameproofing of this resin is carried out in order to cause the mechanical-strength fall of resin, this approach is not practical [this approach], either.

[0006]

[Problem(s) to be Solved by the Invention] while the purpose of this invention has a high fluidity -- the resin of the styrene system of high shock resistance -- developing -- in addition -- and after flameproofing is to offer the fire-resistant resin constituent holding an advanced fluidity and impact strength-proof.

[0007]

[Means for Solving the Problem] When this invention person etc. found out having a very high fluidity and high shock

resistance when a rubber denaturation vinyl aromatic series polymer (Following HIPS and brief sketch) contains the polystyrene obtained by a part of that matrix by the anionic polymerization method more than a constant rate and flameproofing of this HIPS was carried out further, that high fluidity and high shock resistance that it had before flameproofing found out being held on high level, and completed this invention.

[0008] This invention is explained in more detail below. With the rubber denaturation vinyl aromatic series polymer with which the continuous phase consists of resin containing the vinyl aromatic series polymer obtained by the anionic polymerization method which is the component (A) used for this invention Nucleus alkylation styrene [like styrene or O-methyl styrene] whose continuous phase is, Independent or the polymers which are obtained by carrying out the polymerization of two or more sorts of vinyl aromatic series monomers, such as nucleus halogenation styrene like alpha-alkylation styrene like alpha methyl styrene and mono-KURORU styrene, constitute a resin continuous phase. And the polymer component obtained by the anionic polymerization method in the polymer contains, and the styrene system polymer of the rubber reinforcement which the rubber-like polymer is distributing by the shape of a particle as a dispersed phase is said.

[0009] The vinyl aromatic series polymer obtained by the anionic polymerization method used for this invention is a polymer obtained by carrying out the polymerization of the monomers of the above-mentioned styrene system according to an anionic polymerization catalyst, for example, alkyl lithium. The polymerization initiation reaction of anionic polymerization is quick, and the mono dispersion polymer with which chain length gathered is easy to be obtained. Usually, it is possible to be in the living condition which the active metal lithium combined with the polymer end, and to build the star type polymer which has branching structure by making it react with a polyfunctional low molecular weight compound using this activity end. The polymer of the linear structure acquired from the vinyl aromatic series monomer built with these anionic polymerization and the polymer of a stellate pattern are used for this invention.

[0010] It is the branching vinyl aromatic series polymer of the structure indicated to be the vinyl aromatic series polymer component of the letter structure of branching said to this invention to a bottom type.

M-(P) n (M expresses among a formula the branching nucleus of multifunctional-compound residue or polyvinyl aromatic compound residue, and the number of the vinyl aromatic series polymer P with which P is the integer of 3-8, and has combined a vinyl aromatic series polymer and n in M)

Although the number of the arms of the polystyrene of the letter of branching of this invention is 3-8 range, 3-6 pieces are 3-4 pieces still more preferably preferably.

[0011] The content of the vinyl aromatic series polymer obtained by the anionic polymerization method in the vinyl aromatic series polymer which makes a continuous phase is 5 % of the weight or more, and is 20 % of the weight or more still more preferably 10% of the weight or more preferably.

[0012] As for the vinyl aromatic series polymer obtained by the anionic polymerization method contained in the continuous phase of the rubber denaturation vinyl aromatic series polymer of this invention, the structure is included for the thing of linear structure, and the thing of the above-mentioned branching radial structure. The greatest description of especially the thing of linear structure is a narrow thing in molecular weight distribution. Unlike the thing of a radical polymerization method usual in the vinyl aromatic series polymer obtained by the anionic polymerization method, the polymer near mono dispersion is easy to be obtained. for this reason, physical properties -- a bad influence -- ***** -- it is possible to achieve low-molecular-weight-ization of the whole resin continuous phase, without increasing these components, in there being neither an extreme low molecular weight constituent nor a component like oligomer, therefore blending with HIPS of a radical polymerization and introducing the polymer component by anionic polymerization into a resin continuous phase.

[0013] Moreover, the constituent of this invention is a fire-resistant resin constituent, and effectiveness is accepted also from on the fire-resistant engine performance in which it is hard to be dropped at the time of a combustion test when flameproofing of the HIPS with few low molecular weight constituents extreme like **** and oligomer components is carried out.

[0014] HIPS which contains the vinyl aromatic series polymer obtained by the anionic polymerization method of this invention in a continuous phase may adopt what kind of how to make. For example, the approach of blending the vinyl aromatic series polymer of the mono dispersion linear structure compounded by the anionic polymerization method to the usual HIPS. Branching furthermore compounded with the coupling process of anionic polymerization, the approach of blending a radial mold vinyl aromatic series polymer, etc. are mentioned.

[0015] The ratio (molecular-weight-distribution Mw/Mn) of the weight average molecular weight by the gel permeation chromatography differential refractive-index method (it is also called a PGC-RI system) and number average molecular weight is 2.0 or less thing, and the vinyl aromatic series polymer of the linear structure acquired

according to the anionic polymerization used for this invention has weight average molecular weight in the range of 50,000 - 200,000. When molecular weight distribution (M_w/M_n) exceed 2.0, it is the inclination for the mono dispersion nature which is the description of anionic polymerization to be lost, when weight average molecular weight does not fulfill 50,000, the mechanical strengths of resin tend to run short, and in exceeding 200,000, it becomes the inclination for the fluidity which is the description of this invention to be lost.

[0016] The letter vinyl aromatic series polymer of branching of the anionic polymerization of this invention requires that the ratio of the weight average molecular weight M_wL by GPC-light scattering measurement and the apparent-mass average molecular weight M_wR by the GPC-RI system should be 1.2 or more preferably 1.10 or more in the analysis by the gel permeation chromatography (Following GPC and brief sketch) of the continuous phase of the below-mentioned HIPS resin. the degree of the letter vinyl aromatic series polymer of branching -- increasing -- ** -- although a M_wL/M_wR value increases even if the content of the branched polymer which is not is the same -- the case of this invention -- a degree -- at most -- it is eight branching and M_wL/M_wR is four or less preferably five or less from this. the GPC light scattering measurement of the continuous phase of HIPS of the (A) component of this invention -- a basis -- **** weight average molecular weight is in the range of 120,000-500,000 -- desirable -- more -- desirable -- 150,000-300,000 -- it is the range of 150,000-250,000 still more preferably.

[0017] When compounding the letter vinyl aromatic series polymer of branching of the component (A) of this invention with anionic polymerization coupling process, it usually becomes mixture, such as a polymer, at a non-coupling object, a dimer, and a trimer pan. For this reason, even if molecular weight distribution use that with which 1.5 or less chain length gathered as a polymer before coupling, molecular weight distribution tend to spread after a coupling reaction. Therefore, what is necessary is for the range of the molecular weight distribution of the letter vinyl aromatic series polymer of branching of this invention just to be 1.0-3.0. In the case of the letter vinyl aromatic series polymer of branching, molecular weight distribution spread by the coupling reaction, but since a ***** low molecular weight constituent and an oligomer component do not increase a bad influence to physical properties with [the molecular weight distribution of the polymer before coupling] 1.5 [or less], molecular weight distribution may be large to some extent.

[0018] As for the rubber-like polymer which accomplishes the dispersed phase of the (A) component of this invention, the glass transition temperature says a thing -30 degrees C or less. As an example, diene system polymers, such as polybutadiene, a styrene butadiene rubber (SBR), and acrylonitrile-butadiene rubber (NBR), ethylene-propylene-diene rubber (EPDM), acrylic rubber, etc. can be mentioned. Moreover, as polybutadiene rubber, high cis polybutadiene rubber and low cis polybutadiene rubber can be used suitably. The further above-mentioned polybutadiene rubber and the thing to which SBR and NBR hydrogenated a part or all of the partial saturation duplex association are also used.

[0019] Although adjustment of HIPS which accomplishes a part of above-mentioned (A) component is generally obtained by carrying out the radical polymerization of the aforementioned vinyl aromatic series monomer under massive, massive and suspension, or an emulsion-polymerization condition to the bottom of existence of the above-mentioned rubber-like polymer, the approach by the bulk polymerization is excellent in economical efficiency. In addition, when based on a bulk polymerization, ethylbenzene and toluene which are a little inert solvent may be added. The dispersed phase of the structure where a part of vinyl aromatic series monomer carried out the graft to the perimeter of a rubber-like polymer particle by the above-mentioned all directions method by carrying out the polymerization of the vinyl aromatic series monomer to the bottom of existence of a rubber-like polymer, and the particle of some vinyl aromatic series polymers was included inside the rubber-like polymer particle is formed.

[0020] It can dissolve in the good solvent of the vinyl aromatic series polymer which constitutes the continuous phase of a rubber denaturation vinyl aromatic series resin constituent, for example, a methyl ethyl ketone, and judgment extraction of the dispersed phase can be carried out by performing centrifugal separation actuation. furthermore, the mean particle diameter of the dispersed phase which the rubber-like polymer of the (A) component accomplishes -- a law -- according to a method, it is adjusted to the range of 0.1-4.0 micrometers. The range of more desirable particle diameter is 0.4-3.0 micrometers. Moreover, the swelling index (SwellingIndex) to the toluene used as the standard of the degree of cross linking of a dispersed phase particle is adjusted to the range of 6-14.

[0021] The letter vinyl aromatic series polymer of branching by the anionic polymerization method included in the continuous phase of the (A) component of this invention can be efficiently built for example, with anionic polymerization coupling process. It can obtain by specifically carrying out the polymerization of said vinyl aromatic series monomer in a hydrocarbon solvent using an organolithium compound, and carrying out the coupling reaction of the activity piece end vinyl aromatic series polymer obtained with a multifunctional compound. As an organolithium compound of the above-mentioned approach, n-propyl lithium, an iso-propyl lithium, n-butyl lithium, iso-butyl lithium, sec-butyl lithium, tert-butyl lithium, a phenyl lithium, etc. can be raised.

[0022] Moreover, the multifunctional compound used for a coupling reaction is a low molecular weight compound which has 3-8 functional groups which react with an activity lithium end and can form association. As an example of these low molecular weight compounds, the Pori halogenated compound, the Pori epoxy compound, a polycarboxylic acid ester compound, the poly ketone compound, a polycarboxylic acid anhydride, etc. can be raised. Specifically, they are silicon tetra-chloride, $\text{JI (TORIKUROROSHIRIRIRU)}$ ethane, 1 and 3, 5-TORIBUROMO benzene, methyl TORIKURORO tin, epoxidized soybean oil, tetraglycidyl ether 1, a 3-bis-aminomethyl cyclohexane, oxalic acid dimethyl, trimellitic acid tree 2-ethylhexyl, pyromellitic acid tetramethyl, 2, 3-JIASETO nitril cyclohexanone, pyromellitic acid 2 anhydride, etc..

[0023] Said lithium compound is [as opposed to / in case the above-mentioned anionic polymerization is carried out / the vinyl aromatic series monomer 100 weight section] 0.01 - 1.0 weight *****. Moreover, the above-mentioned multifunctional compound carries out equivalent addition 0.5 to 1.5 times, and is made to react to an organic lithium. A reaction advances promptly and is usually completed in several 10 minutes from several minutes. A cyclohexane, n-hexane, benzene, toluene, ethylbenzene, THF, etc. are used as the above-mentioned reaction solvent. As reaction temperature which carries out the above-mentioned anionic polymerization, it carries out in -30-120 degrees C. Moreover, although polymerization time amount is based also on the solvent to be used or polymerization temperature, it is usually several seconds - several hours.

[0024] The vinyl aromatic series polymer of many branching is compoundable by using an organolithium compound for an initiator, carrying out the polymerization of the vinyl aromatic series monomer in a hydrocarbon solvent apart from the above-mentioned coupling reaction, adding a small amount of polyfunctional vinyl aromatic series monomer (for example, divinylbenzene) as a polymerization initiator, and carrying out the polymerization of the piece end activity vinyl aromatic series polymer which exists in the state of after [a polymerization conclusion] living. The range of the rate of the polyfunctional monomer added in this approach is 0.1-1.0 to an organic lithium in a mole ratio. By this approach, the branched polymer near a star type polymer of molecular weight distribution is got by the real target of a little large many branching.

[0025] Next, the analysis approach of the letter vinyl aromatic series polymer of branching used by this invention is explained. It is the molecular weight by which ***** count is carried out at the elution time amount and the calibration curve of the relation of molecular weight which were created using the mono dispersion polystyrene which classified styrene resin with molecule size, detected styrene resin concentration using the concentration detector, for example, a differential refractive index detector, and was manufactured according to anionic polymerization on the other hand in measurement of the molecular weight of common styrene resin by the gel permeation chromatography. However, since the polymer which has branching flows out late round [a chain / tend] in a GPC solvent, the molecular weight measured with the above-mentioned GPC differential refractive index detector gives measured value smaller than actual molecular weight.

[0026] It carries out because it is in the analysis of the letter polystyrene of branching of this invention with both GPC-light scattering measurement and a GPC differential refractive-index method. if light is hit to a solution with GPC-light scattering measurement -- the solute in a solution -- a basis -- fluctuation by the scattered light of ***** is measured. As for this fluctuation, fluctuation serves as size, so that a solute molecule is a macromolecule owing to the thermal motion of a solute molecule. Extent of this fluctuation is observed with the dilute solution, and the principle of the determination of molecular weight by light scattering measurement (GPC-LALLS law) measures molecular size. In GPC-light scattering measurement, if it is the same molecular weight, even if it is not based on molecule size, but elution locations differ, the same molecular weight is given.

[0027] Whenever [branching] is called for from the jump of molecular weight by measuring MwL by the GPC-light scattering measurement of the polymer which is made to put in and carry out the coupling reaction of the coupling agent to the prepolymer and it which carried out the polymerization with butyl lithium by anionic polymerization, and is obtained, respectively. The sample to which the blend ratio of branched polymer and a linear polymer was changed using the linear polydisperse polymer of the radical polymerization considered that linear mono dispersion polymer ** of whenever [branching], the branched polymer of molecular weight known, and anionic polymerization does not almost have branching is adjusted, and MwR by MwL and the GPC-RI system by GPC-light scattering measurement is measured. Since it becomes such a big value that there are many branching components in a polymer, MwL/MwR serves as an index which shows the amount of the polymer component of branching in a sample.

[0028] A ***** calibration curve can be created to weight % of the branched polymer in a blend object, and the value of MwL/MwR. It is possible to get to know the concentration of the branched polymer in a strange sample using this calibration curve. A sample is dissolved using the good solvent of polymers, such as MEK, as analytical method from a fire-resistant resin constituent, a part for the insoluble solution of minerals, such as gel in a constituent and an antimony

trioxide, etc. is removed by centrifugal separation, solvents, such as alcohol, are used for extractives, a flame retarder and a polymer are separated, and the quantum of a branching component can do this polymer by carrying out the above-mentioned GPC analysis.

[0029] the flame retarder used as a (B) component of this invention -- a halogen series flame retardant -- and -- or a phosphorus series flame retardant is said and what contains antimony oxide if needed is said. As a halogen series flame retardant used for this invention, a halogenation bisphenol, an aromatic series halogenated compound, a halogenation polycarbonate, a halogenated-aromatics vinyl system polymer, halogenation SHIANU rate resin, halogenation polyphenylene ether resin, etc. are mentioned.

[0030] Preferably Deca bromine diphenyloxide, the oligomer of tetra-bromine bisphenol A, Bromine-ized bisphenol system phenoxy resin, a bromine-ized bisphenol system polycarbonate, bromine-ized polystyrene, bromine-ized bridge formation polystyrene, etc. -- it is -- as the concrete example of halogenation bisphenols -- a jib -- ROM bisphenol A -- Tetra-bromine bisphenol A, the dichlorobis phenol A, tetra-chloro bisphenol A, a jib -- the ROM bisphenol F, the tetra-bromine bisphenol F, the dichlorobis phenol F, the tetra-chloro bisphenol F, and a jib -- the ROM bisphenol S, the tetra-bromine bisphenol S, the dichlorobis phenol S, the tetra-chloro bisphenol S, etc. are mentioned.

[0031] The organic phosphorous compounds used for this invention are a phosphine, phosphine oxide, a BIHOSU fin, phosphonium salt, phosphinate, phosphoric ester, phosphite, etc. They are more specifically triphenyl phosphate, methyl neopentyl phosphate, pentaerythritoldiethyldiphosphite, a methyl neopentyl FOSU fight, a phenyl neopentyl FOSU fight, pentaerythritol JIFENIRUJI phosphate, JISHIKURO pentyl hypo phosphate, dineopentyl hypophosphite, a phenyl pyrocatechol FOSU fight, an ethyl pyrocatechol FOSU fight, and JIPIRO catechol HAIPOJI phosphate.

[0032] Aromatic series system mono-phosphoric ester and aromatic series system condensed-phosphoric-acid ester are desirable especially as an organic phosphorous compound. Also in phosphoric ester, as aromatic series system mono-phosphoric ester, it is desirable in triphenyl phosphate and tricresyl phosphate **, and concomitant use of aromatic series system mono-phosphoric ester and aromatic series system condensed-phosphoric-acid ester is [from / after that volatility-proof shock resistance, thermal resistance, and a fluidity balance] desirable.

[0033] The antimony oxide used if needed as a (B) component of this invention is used when using a halogen series flame retardant as a (B) component. Antimony oxide acts effectively as a fire-resistant assistant, when a halogen-containing compound is used as a flame retarder. As antimony oxide, they are an antimony trioxide, antimony tetroxide, and antimony pentoxide. Antimony oxide is added five to 50% of the weight to a halogen series flame retardant.

[0034] This invention has not prescribed especially the fire-resistant engine performance or the flame resistance ability itself of a fire-resistant resin constituent. By making more than the amount of specification of the vinyl aromatic series polymer component by the anionic polymerization method contain as a resin matrix component, the effectiveness of this invention has the few falls of the physical properties which pose a problem by performing flameproofing processing, and is in the point that the fire-resistant resin constituent which is excellent in the balance of a fluidity and physical properties as a result is obtained. That is, it responds to the amount of the flame retarder to add, and is vertical of the flame resistance trial specification of UL94. It is possible to make and divide the presentation to which it is satisfied with the burning method of 94V-0 (under non-**), 94V-1 (being un-dropped), and 94V-2 (dropping), and also when it is any, the fire-resistant resin constituent which was able to balance the fluidity and the mechanical strength is obtained.

[0035] (A) Well-known equipment, for example, a kneader, a Banbury mixer, and ***** carry out melting kneading of the mixing of a component and the (B) component with a twin screw extruder etc. To a fire-resistant resin constituent, additives, such as stabilizers, such as a higher fatty acid, a higher-fatty-acid metal salt, poly dimethylsiloxane, and a hindered phenol, a pigment, a plasticizer, and an antistatic agent, can be added if needed.

[0036]

[Embodiment of the Invention] Hereafter, although an example explains this invention in more detail, these do not restrict the range of this invention at all. The measurement in ****, an example, and the example of a comparison followed the approach of describing below.

(1) It measured at 23 degrees C by the approach based on Izod impact test ASTM-D256.

(A V notch, 1/8 inch test piece)

(2) It measured by the approach based on BIKATTO softening temperature ASTM-D1525, and considered as the heat-resistant scale.

(3) It measured by the approach based on ASTM-D1238 as an index of a melt flow rate (MFR) fluidity. It asked from the amount of extrusion per 10 minutes (g / 10 minutes) on 5kg of loads, and conditions with a melting temperature of 200 degrees C.

[0037] (4) The VB (vertical burning) method based on evaluation UL-94 which are fire retardancy estimates (1/8 inch test piece).

(5) It measured by 5 degrees of diffusion angles, light source: 5mw (helium-Ne laser), the temperature of 38 degrees C, the solvent tetrahydrofuran, sample concentration 0.1 wt/v%, and sampling pitches 1/0.4 (time/second), using the TOSOH CORP. make (HLC-8020, differential refractive index detector internal organs), a company separation column (three TSKgel-GMHXL being used), and a company light-scattering detector (LS-8000) as an analysis GPC chromatograph of measurement of molecular weight, and the letter vinyl aromatic series polymer of branching.

[0038] Each component used in an example and the example of a comparison used what was adjusted in the following examples of reference.

The example 1 (adjustment of radical polymerization rubber denaturation polystyrene A1) of reference Polybutadiene (the Nippon Zeon Co., Ltd. make, NIPORU 1220SL) was dissolved in styrene, and ethylbenzene and the polymerization undiluted solution of the following presentation of t-butylperoxyisopropylcarbonate on the little **** and last target were prepared. (Unit: Weight section)

- Polybutadiene 9.8 and styrene 76.8 and ethylbenzene 13.0 and t-butylperoxyisopropylcarbonate 0.04 and alpha-methyl-styrene dimer 0.02 and poly dimethylsiloxane 0.10 [0039] Each content volume sent the above-mentioned polymerization undiluted solution continuously at 2.2l. / hr to 3 tub type reaction machine with an agitator which is 6.2l. Reaction inside-of-a-plane temperature was adjusted so that the solid content concentration of the first reaction machine outlet might become 38% of the weight. Furthermore, the solid content concentration of the third reaction machine outlet controlled the reaction machine internal temperature to become 80% of the weight. Subsequently, it sent into the devolatilizer under 230 degrees C and a vacuum, unreacted styrene and ethylbenzene were removed, it corned with the extruder, and the rubber denaturation polystyrene A1 of a pellet type was obtained. The rate of the polybutadiene in A1 was 12.3 % of the weight. The dispersed phase weight found from a part for the insoluble solution of the methyl ethyl ketone of A1 was 30 % of the weight, and the continuous phase was 70 % of the weight. Moreover, the weight average molecular weight and number average molecular weight of a continuous phase which were calculated from GPC of methyl-ethyl-ketone extractives were 220,000 and 81,000, respectively. The mean particle diameter of a **** dispersed phase was 1.5 micrometers, and the swelling index to toluene was 9.5.

[0040] The example 2 (adjustment of the letter polystyrene B1 of branching, and B-2) of reference

The brewing internal temperature was controlled for styrene 7.0kg and cyclohexane 35kg at 55 degrees C in the autoclave with an induction agitator which carried out the nitrogen purge. Agitating at high speed, 10%THF solution containing n-butyl lithium 12.6g was driven in, and the reaction was started. The reaction-after 5 minutes machine internal temperature rose at 87 degrees C. Carried out the little sampling of the reaction mixture, it was made to precipitate in a methanol, and the reaction was stopped. The weight average molecular weight of pre BORIMA before a coupling reaction was 54,000, number average molecular weight was 52,000, and it was Mw/Mn=1.038.

Subsequently, as a coupling agent, 20%THF solution containing tetraglycidyl ether 1 and 16g (it outlines Following TED.) of 3-bis-aminomethyl cyclohexanes was driven in, and the coupling reaction was started. The reaction machine internal temperature was controlled at 70 degrees C, and the coupling reaction was performed for 20 minutes. Reaction mixture was taken out in a lot of methanols, and the letter polystyrene B1 of branching was collected. GPC of this thing to weight average molecular weight was 137,000, and number average molecular weight was 110,000.

[0041] The GPC chart was as having been shown in drawing 1, and was 2 crest distribution of the low-molecular-weight polymer of non-coupling in part with the coupling polymer which carried out macromolecule quantification by TED coupling. The weight average molecular weight of the amount component of macromolecules was 155,000, and since the weight average molecular weight of a low-molecular non-coupling component was 54,000, it was checked that the polystyrene of trifurcation structure had been obtained by TED coupling. The reason the polymer of trifurcation is formed of TED of **** 4 functionality is considered because the polystyrene of end activity cannot react to the 4th epoxy group easily because of steric hindrance. The content of trifurcation HORIMA was 87 % of the weight from the surface ratio of the chromatogram of a macromolecule component and a low-molecular component.

[0042] By adjusting the amount of placing of n-butyl lithium which is a polymerization catalyst like the example 2 of reference, that to which the weight average molecular weight of the prepolymer before coupling was changed was adjusted, and trifurcation polymer B-2 from which the coupling reaction by TED is performed and molecular weight differs was obtained. The branching result and melt flow rate of B-2 are described in Table 1.

[0043] The example 3 (adjustment of the letter polystyrene B3 of 4 branching, and B4) of reference

Cyclohexane 6kg and a styrene monomer 1.0kg brewing ** internal temperature were controlled at 55 degrees C to the autoclave which carried out the nitrogen purge. Subsequently, 10%THF solution containing n-butyl lithium 1.57g was driven in, and the polymerization was started. The reaction-after 5 minutes machine internal temperature rose at 83

degrees C. After continuing a reaction for 20 minutes, a part of reaction mixture was sampled, and GPC measurement was carried out. The weight average molecular weight of this thing was 67,400. Subsequently, 20%THF solution containing JI (TORIKUOROSHIRIRIRU) ethane 0.82g was driven in, and the coupling reaction of the internal temperature was controlled and carried out to 70 degrees C for 20 minutes. It processed like the example 2 of reference, and the letter polystyrene B3 of branching was obtained. The weight average molecular weight of Mw of this thing was 272,000, and non-coupling was a trace. Mw/Mn of this thing is 1.05, is polystyrene of 4 branching structures near mono dispersion, and is *****. The reason the polystyrene of 4 branching structures was obtained using the coupling agent of six organic functions is also considered very much for being hard to react by steric hindrance like the time of using TED for a coupling agent beyond 4 branching structures.

[0044] The 6kg cyclohexane and the 1.0kg styrene monomer were made to react using the charge of brewing n-butyl lithium 1.5 times, and JI (TORIKUOROSHIRIRIRU) ethane 1.1g was made to use and react to a coupling agent like the polymer of B3. Polystyrene B4 of 4 branching structures of front [coupling] polymer weight-average-molecular-weight 49,400 and weight-average-molecular-weight 202,000 after coupling was obtained.

[0045] The example 4 (adjustment of linear mono dispersion polystyrene L1 and L2) of reference Cyclohexane 6.0kg and a styrene monomer 1.0kg brewing internal temperature were made the autoclave at 40 degrees C. Subsequently, 20% cyclohexane solution which contains n-butyl lithium 0.52g as a polymerization initiator was driven in, agitating violently. The after [5 minutes] internal temperature rose at 65 degrees C. Churning was continued for after [exoergic termination] 20 minutes, subsequently to a lot of methanols reaction mixture was opened, and linear polystyrene L1 was obtained. The weight average molecular weight Mw of L1 was 205,000, and Mw/Mn was 1.02. Similarly, only the addition of n-butyl lithium was set to 0.90g, and Mw132,000 and the linear polystyrene L2 near the mono dispersion of Mw/Mn=1.08 were obtained.

[0046] The example 5 (adjustment of linear polydispersed polystyrene L3 and L4) of reference The polymerization undiluted solution which becomes 3 tub type reaction machine used for adjustment of rubber denaturation polystyrene A1 from styrene and ethylbenzene was sent continuously, and linear mold polystyrene and L3 were obtained by thermal polymerization initiation. An analysis result and the value of a melt flow rate are shown in Table 1. On the other hand, the polymerization undiluted solution which becomes a complete-mixing mold reaction machine from styrene, ethylbenzene, an alpha-methyl-styrene dimer, and t-butylperoxyisopropylcarbonate was sent continuously, and linear mold polystyrene and L4 were obtained. An analysis result and the value of a melt flow rate are shown in Table 1.

Bromine-ized epoxy resin: F55 bromine content 59.0wt% made from Asahi Tiba [0047]

[Table 1]

表 1

ポリスチレン サンプル	重量平均分子量 Mw × 10 ⁴	数平均分子量 Mn × 10 ⁴	分子量分布 Mw/Mn	*メルトフロート (g/10min)
B1 アニオン3分枝	13.7	11.0	1.24	44.6
B2 アニオン3分枝	15.2	12.5	1.23	32.1
B3 アニオン4分枝	27.2	25.9	1.05	14.0
B4 アニオン4分枝	20.2	18.5	1.09	25.2
L1 アニオン直鎖	20.5	20.1	1.02	3.4
L2 アニオン直鎖	13.2	12.2	1.08	20.2
L3 ラジカル直鎖	18.0	8.61	2.09	9.0
L4 ラジカル直鎖	25.0	11.3	2.21	2.5

*ISO-R1133に準拠
(200℃、5kg荷重)

[0048] The example 6 (quantum of the letter vinyl aromatic series polymer of branching) of reference TED was used for the coupling agent like the example 2 of reference in order to perform the quantum of the letter PS of branching in a polymer sample, and MwL198,000 and the trifurcation mono dispersion polymer (B-7) of Mw/Mn=1.09 were adjusted. MwL207,000 with near B-7 and molecular weight and the polydispersed polystyrene

Asahi Chemical polystyrene GP680 of marketing of Mw/Mn=2.00 are used, and it is B-7/(B-7+680) x102. It is made to dissolve in THF at a rate of 0, 5, 10, 30, and 50,100. GPCLALLS, MwLMwR is measured using GPCRI, respectively and it is MwL/MwR to an axis of abscissa in an axis of ordinate B-7/(B-7+680) x102. It took, the calibration curve was created and drawing 2 was obtained. (The reason using a trifurcation polymer is because it becomes smaller than the case where a trifurcation polymer uses a polymer with many other degrees to the value of MwL/MwR with few [therefore] degrees most in this invention here) .

[0049]

[Example]

The radical polymerization rubber denaturation polystyrene A1 adjusted in examples 1-8 and the example 1 of a comparison - the example 1 of 2 reference, the polystyrene adjusted in the example of reference, and a flame retarder were blended by the presentation of Table 2, and using the twin screw extruder, melting kneading was carried out, it pelletized, and the fire-resistant resin constituent of this invention was adjusted. Subsequently, the obtained fire-resistant resin constituent was fabricated with the injection molding machine with the resin temperature of 220 degrees C, the test piece was created, and physical properties were evaluated. The evaluation result of each test piece is shown in Table 2.

[0050]

[Table 2]

表 2

実施例、比較例	実 施 例								比 較 例	
	1	2	3	4	5	6	7	8	1	2
組成物の名称	C1	C2	C3	C4	C5	C6	C7	C8	H1	H2
ラジカル重合 ゴム変性 ポリスチレン	70	70	70	60	70	60	60	60	70	60
B1 B2 B3 B4 L1 L2 L3 L4	30	30	30	40	30	40	40	40	30	40
ゴム変性ビニル 芳香族重合体(A) の遠鏡相の MwL/MwR	1.41	1.4	1.45	1.53	1.04	1.04	1.60	1.60	1.03	1.08
難燃剤(B) ブロム化ポリスチレン (パイロチェック68PB) ブロム化エポキシ樹脂	22	22	20	20	20	20	22	17	22	22
トリフェニルホス フェート(TTP)			5	5				5		
Sb ₂ O ₃	5	5	5	5	5	5	5	5	5	5
物性評価 アイソット衝撃強度 kg·cm/c	7.2	8	7.8	5.8	6.7	4.0	5.8	6.0	6.2	4.3
デュボンダート強さ 2mm kgf·c	32	45	22	23	8.2	5.5	28	25	10.0	5.1
MFR g/10 min	53.0	47.0	28.0	32.0	8.8	15.3	54	62	6.5	3.8
UL94 vertical burning法	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0

[0051]

[Effect of the Invention] The fire-resistant resin constituent of this invention which contains the vinyl aromatic series resinous principle by the anionic polymerization method in a resin matrix has **** profit and fire retardancy which were shown in the example and the example of a comparison, and is excellent in the balance of a fluidity and a

mechanical strength. The constituent of this invention is suitable for household-electric-appliances components, OA machine vessel part article, etc. of which fire retardancy is required, and the role played in these industrial worlds is large.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The fire-resistant resin constituent characterized by consisting of the rubber denaturation vinyl aromatic series polymer 99 with which the continuous phase consists of resin containing the vinyl aromatic series polymer obtained according to component (A) anionic polymerization - the 50 weight sections, and the component (B) flame retarder 1 - 50 weight sections.

[Claim 2] The fire-resistant resin constituent according to claim 1 whose vinyl aromatic series polymer obtained according to the anionic polymerization of a component (A) is a vinyl aromatic series polymer of the linear structure where the ratio of the weight average molecular weight by the gel permeation chromatography differential refractive-index method and number average molecular weight is 2.0 or less, and weight average molecular weight is 50,000 - 200,000.

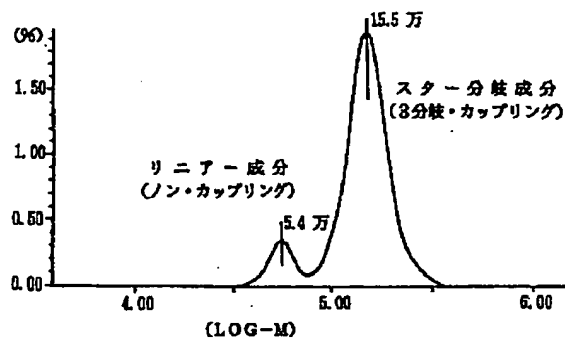
[Claim 3] The fire-resistant resin constituent according to claim 1 whose ratio of the weight average molecular weight MwL according [the vinyl aromatic series polymer obtained according to the anionic polymerization of a component (A)] to gel permeation chromatography light scattering measurement and the weight average molecular weight MwR by the gel permeation chromatography differential refractive-index method is 5.0 or less or more 1.10 letter vinyl aromatic series polymer of branching.

[Claim 4] For the branch polymer P, 120,000-500,000, and a molecular weight distribution (Mw/Mn) are the fire-resistant resin constituent given [a given molecular weight distribution (Mw/Mn) is the vinyl aromatic series polymer with which the letter vinyl aromatic series polymerization object of branching is the structure shown by the bottom formula, and 1.5 or less chain length gathered] in claim 3 term given weight average molecular weight is the letter vinyl aromatic series polymer of branching of 1.0-3.0.

M-(P) n (M expresses among a formula the branching nucleus of polyfunctional residue or polyvinyl aromatic compound residue, and the number of the vinyl aromatic series polymer with which P is the integer of 3-8, and has combined a vinyl aromatic series polymer and n with M)

[Claim 5] The fire-resistant resin constituent according to claim 1 to 4 whose flame retarders of a component (B) are a halogen series flame retardant, a halogen series flame retardant, antimony oxide, and a system flame retarder that is not stretched again.

[Translation done.]

Drawing selection drawing 1 ☒

[Translation done.]